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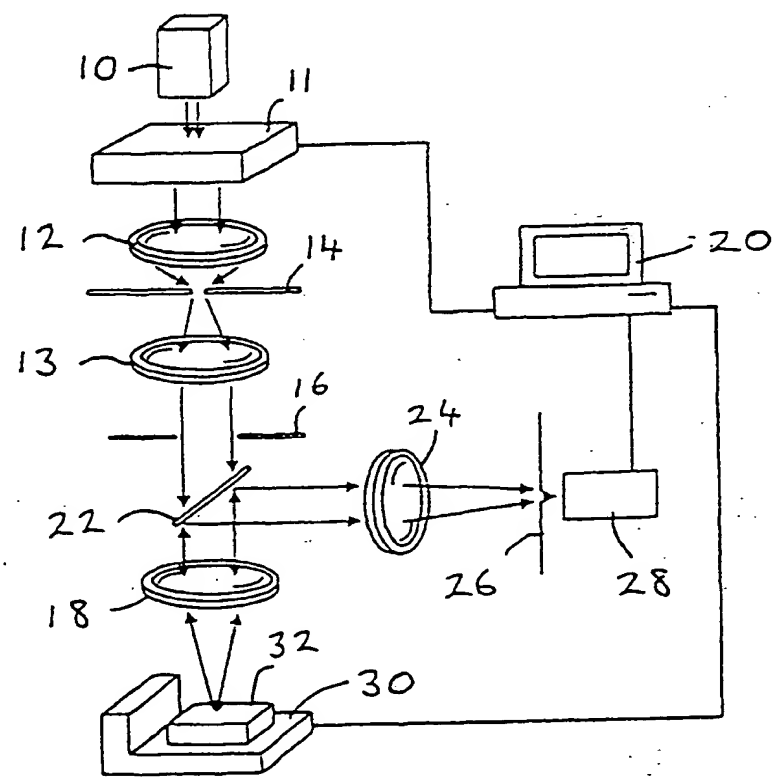
(57) Abstract

A method of erasable/rewritable optical data storage is provided in which a laser beam from a laser (10) operated in either a pulsed or continuous wave mode is focussed by an optical system (11–18) onto a photorefractive polymeric material (32) to cause two photon excitation of the material to record data which may subsequently be erased by illuminating the material with radiation having a wavelength in the ultraviolet or visible spectrum to erase the recorded data. New photorefractive polymeric materials having a relatively narrow absorption band for use in the method are also disclosed.



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ERASABLE/REWRITABLE OPTICAL DATA STORAGE WITH PHOTOREFRACTIVE POLYMERS

This invention relates to optical data storage and more particularly to erasable/rewritable three-dimensional optical data storage with photorefractive polymers.

Multi-layered (or three-dimensional) optical memories have increasingly become a field of interest in the development of high-density optical data storage devices. Systems that utilise multiple layer recording can achieve recording densities from 100 to 10,000 times higher than conventional optical data storage devices.

The use of two-photon excitation in three-dimensional (3D) bit optical data storage has grown due to its ability to increase the density in a given material by reducing the volume of the recorded bit. The probability of two-photon excitation is proportional to the squared intensity of the incident light; this effect produces excitation only within a small region of the focus spot. As a result there is less cross talk between neighbouring data layers. Another advantage of two-photon excitation is the reduction of multiple scattering because of the utilisation of an illumination beam of an infrared wavelength, so that more layers can be recorded along the depth of a volume material.

Over the years different materials have been used for 3D bit data storage under two-photon excitation. Two-photon 3D bits recorded in photopolymerizable and photobleaching materials have demonstrated that recording densities could reach terabits per cubic centimeter; unfortunately both materials are not erasable. U.S. Patent No. 5,289,407 assigned to Cornell Research Foundation, Inc. discloses a method of 3D optical data storage in which a beam of coherent light is used to cause two-photon photopolymerization of a specimen gel to produce a bead of polymerised material in the gel which has a different refractive index from the surrounding gel material. However, this change is irreversible, and so the data bits are not erasable.

Photochromic materials that undergo a change in isomer states and photochromic polymers that produce a change in refractive-index upon two-photon excitation are both erasable materials. Another type of material that is of considerable interest is photorefractive material. The photorefractive effect results in a modulation of the refractive-index at the point of focus induced by the spatial distribution of electric charges upon illumination.

It has been discovered that such a change in the refractive index in photorefractive material may be reversed by illuminating the medium again with radiation to produce a uniform redistribution of the electric charges and erase the recorded information. However, this has previously only been achieved in a photorefractive crystals, e.g. lithium niobate ($LiNbO_3$), which are expensive to manufacture.

It is therefore desirable to provide a method of writing and erasing optical data in relatively inexpensive materials.

According to one aspect of the invention, there is provided a method of writing and erasing optical data comprising:

producing a beam of focusable, coherent light;

focussing the beam on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

According to another aspect of the invention there is provided a method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing a beam of coherent light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing another beam of coherent light on the photorefractive material to cause two-photon excitation of the material at the focal point of the beam

thereby modulating the refractive index at the focal point to re-write data in the photorefractive material.

– In the method of the present invention, the two-photon excitation produces a change in the spacial distribution of the electric charges at the focal point, thereby modulating the refractive index of the material at the focal point.

Preferably, the photorefractive polymeric material used in the method is such that illumination with electro-magnetic radiation in the ultraviolet (UV) or visible spectrum produces a uniform redistribution of the spacial distribution of the electric charges forming the data bits to erase the recorded data. The photorefractive polymer is preferably arranged to absorb radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum. Creating a narrow absorption band will decrease the materials susceptibility to deterioration from the reading process or from incidental ultraviolet light (e.g. from sunlight).

A laser may be used in a pulsed mode or a continuous wave laser may be used to write data by two-photon excitation of a photorefractive material. An ultrashort pulsed laser beam is typically used for two-photon exitation because the cooperative nature of two-photon excitation requires the use of a high peak power laser to produce efficient excitation. However, the use of an ultrashort pulse laser increases the cost of a recording device and makes it difficult to produce a compact system. We have also demonstrated that two-photon excitation under continuous wave (CW) illumination is possible. Although the average power needed for CW excitation is increased by approximately two orders of magnitude compared with ultrashort pulsed illumination, the use of continuous wave illumination can enable a fast, low cost, compact erasable two-photon 3D bit optical data storage system to be achieved.

The photorefractive material preferably includes a chromophore which provides absorption in the UV to visible region. The polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum. In one embodiment, the polymer may comprise poly (N-vinylcarbazole) (PVK). In another preferred

embodiment, the polymer may comprise poly (methyl methacrylate) (PMMA). Each of these polymers may be doped with a photosensitive material, such as 2, 4, 7 – trinitro – 9 –fluorenone (TNF). One preferred chromophore is 2, 5 – dimethyl – 4 – (p – nitrophenylazo) anisole (DMNPAA) which also provides absorption and an electro-optical effect in the UV to visible region. The polymeric material may also include a plasticiser, such as N-ethylcarbazole, (ECZ) to reduce the glass transition temperature of the material.

In the present invention, recorded bits of data may be read by employing a confocal microscope, a differential interference contrast (DIC) microscope and/or a phase microscope utilising a source of coherent light of a wavelength on the edge of or outside the absorption band of the photorefractive polymeric material.

According to a further aspect of the invention there is provided a photorefractive polymeric material for use in a method of erasable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the photorefractive material is such as to enable the recording of bits of data by two photon excitation, the reading of the bits of data by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band. The polymeric material preferably comprises a polymer, such as PVK or PMMA. The material may include a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum. Optionally, the polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum, and a plasticiser may be added to reduce the glass transition temperature of the material.

Preferably, a new photorefractive polymeric material in accordance with the second aspect of the invention includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material:

25% - 100% of a polymer, such as PVK or PMMA;

0% - 60% of a chromophore, such as DMNPAA;

0% - 5% of a photosensitive material, such as TNF; and

0% - 40% of a plasticiser, such as ECZ.

Preferred embodiments of the present invention using cheap photorefractive polymers as recording materials for rewritable/erasable 3D bit optical data storage under two-photon excitation to produce a high-density 3D optical data storage system will now be described by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the absorption curve of a photorefractive polymeric material for use in the present invention;

Figure 2 is a schematic diagram of a two-photon excitation microscope used to record data bits in a photorefractive polymer;

Figure 3(a) is a 24 x 24 bit pattern of the letter "C" recorded by two-photon excitation in a photorefractive polymer PVK upon its first reading;

Figure 3(b) is the same region after reading 500 times;

Figure 3(c) is a 24 x 24 bit pattern of the letter "A";

Figure 3(d) is the same region as Figure 3(c) after being exposed to UV illumination showing complete erasure of the recorded information;

Figure 4 shows recorded 24 x 24 bit patterns at different depths in the photorefractive polymer PVK using two-photon excitation;

Figure 4(a) shows a first layer including letter "A";

Figure 4(b) shows a second layer including letter "B" and

Figure 4(c) shows a third layer including letter "C";

Figure 5 (a) is a bit pattern of the letter "E" recorded by two-photon excitation in another photorefractive polymer (PMMA).

Figure 5 (b) is the same region as Figure 5(a) after being exposed to UV illumination showing erasure of the recorded information;

Figure 5(c) is a bit pattern of the letter "F" written into the same area as Figures 1 and 2;

Figure 6 shows recorded bit patterns at different depths in the photorefractive polymer PMMA using two-photon excitation;

– Figure 6(a) shows a first layer including letter "A";

Figure 6 (b) shows a second layer including letter "B" and

Figure 6(c) shows a third layer including letter "C".

One example of a new photorefractive polymetric material that has been used to demonstrate rewritable/erasable 3D bit optical data storage is the polymer poly (*N*-vinylcarbazole (PVK) doped with the photosensitive material 2, 4, 7-trinitro-9-fluorenone (TNF) which provides absorption in the UV to visible region of the spectrum. The photorefractive material also included, as a chromophore, 2, 5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA) which also provides absorption in the UV to visible region. In this experiment compared with previous experiments the randomly oriented chromophores were not aligned by applying an electric field (poling) during polymerisation and operation. Poling of the material requires the creation of a magnetic field across the surfaces of the polymer. Such a uniform magnetic field is difficult to maintain across the surface of a larege polymer sample, increasing the complexity in fabricating the new photorefractive polymer. Finally *N*-ethylcarbazole (ECZ) was added to reduce the glass transition temperature of the material. One preferred concentration of the materials DMNPAA:PVK:ECZ:TNF is 50:33:16:1 by percentage weight of the toral weight of the photorefractive material although it will be appreciated that different proportions of the constituent materials may be used within the ranges specified above. Uniforms films of thickness 100μm were fabricated by combining all the materials in a teflon cast then polymerising the PVK at a temperature of 90°C over 2 days. The resulting polymer block was cut and polished to produce the sample used in the experiments.

Another example of a new photorefractive polymeric material that has been used to demonstrate rewritable/erasable 3D bit optical data storage is the polymer poly (methyl methacrylate) (PMMA) doped with the photosensitive

material 2, 4, 7-trinitro-9-fluorenone (TNF) which provides absorption in the UV to visible region of the spectrum. The photorefractive material also included, as a chromophore, 2, 5-dimethyl-4-(p-nitrophenylazo)anisole (DMNPAA) which also provides absorption in the UV to visible region. In this experiment the randomly orientated chromophores were not aligned by applying an electric field (poling) during polymerisation and operation. Such a poling electric field is not necessary because the local electric field in the focus produced by a high numerical aperture objective is five orders of magnitude greater than that of the incident beam over the objective aperture. This local electric field is strong enough to induce a detectable electro-optic effect.

Finally N-ethylcarbazole (ECZ) was added to reduce the glass transition temperature of the material. One preferred concentration of the materials DMNPAA:PMMA:ECZ:TNF used was 10:73:16:1 by percentage weight of the total weight of the photorefractive material although it will be appreciated that different proportions of the constituent materials may be used within the ranges specified above. Uniform films of thickness 100μm were fabricated by combining all the materials in a teflon cast then polymerising the PMMA at a temperature of 65°C over 2 days. The resulting polymer block was cut and polished to produce the sample used in the experiments.

Figure 1 illustrates the absorption band of a 100μm thick sample of the new photorefractive polymeric materials based on PVK as detected in an Oriel UV-Vis spectrophotometer using a Xenon arc lamp source. The absorbtion band of the photorefractive polymeric material based on PMMA is almost identical.

It is seen from Figure 1 that the maximum of the absorption band of the new materials is within 380-600 nm. Therefore a laser beam of an infrared wavelength at 800 nm can be used in the recording process to produce two-photon excitation at 400 nm. The wavelength for recording may fall substantially within the range from about 750 nm to about 1200 nm. Since the absorption band cuts off approximately at a wavelength of 630 nm, a range of wavelengths from about 630 nm to about 1200 nm can be chosen to read out the

recorded photorefractive data bits without suffering from single-or two-photon excitation. Wavelengths above about 750 nm can be used provided the power of the reading beam is sufficiently low as not to cause single or two-photon excitation.

Referring to Figure 2, there is illustrated an optical system for two photon recording of bits of data in the photorefractive polymeric materials. The recording system comprises a laser (10), a mechanical shutter (11), linked to a computer (20), lenses (12, 13), a pin hole aperture (14), another aperture (16), and an objective lens (18). For reading with confocal geometry, the system also includes a beam splitter (22), a further lens (24), another pin hole aperture (26) and a detector (28) also linked to the computer (20). A three-dimensional scanning stage (30) is provided for the mounting of the sample of photorefractive material (32). The scanning stage (30) is movable in the x, y and z directions under the control of the computer (20).

In the recording process, a Spectra-Physics Tsunami Ti:sapphire laser (10), was focused into the photorefractive polymer sample (32). The laser was used in a pulsed mode to record the bit patterns of Figures 3 and 4 in the PVK photorefractive polymeric material. In mode-locking operation, the laser can produce an ultrashort pulsed beam with a pulse width of 80 fs and an average power of 800 mW. The laser was operated in a continuous wave (CW) mode to record the bit patterns of Figures 5 and 6 in the PMMA photorefractive polymeric material. In each case, the wavelength of the laser was tuned to 800 nm, which approximately corresponds to twice the wavelength of the main absorption band of the sample. From the absorption curve in Figure 1, we can see that there will be no single-photon absorption at a wavelength of 800 nm; only the two-photon absorption can occur at a wavelength of 400 nm. The logic state of the recorded information was controlled by the mechanical shutter (11) linked to the computer (20). The recording material (32) was mounted upon a Melles Griot computer-controlled 3D translation stage (30). For recording, a Zeiss Fluar objective (Figures 3 and 4) and an Olympus UPlanAPO objective

(Figures 5 and 6) (18) with numerical apertures of 0.75 and 0.70 respectively and magnification factors of 20 were used.

– For reading the change in refractive-index caused by the two-photon photorefractive effect an Olympus Fluo View microscope was employed and used in a differential interference contrast (DIC) mode. A He-Ne laser of wavelength 632.8 nm was coupled into the Fluo View for reading the recorded information, as the wavelength of 632.8 nm is on the edge of the absorption band and causes minimal damage to the recorded information (see Fig. 1). To erase the recorded information the region of interest was illuminated with the UV line of a mercury lamp in the Fluo View microscope. In both the reading and erasing an Olympus UPlanAPO objective (18) either with a numerical aperture of 0.7 and a magnification factor of 20 (Figures 3 and 4) or with a numerical aperture of 0.4 and a magnification factor of 10 (Figures 5 and 6) was used.

As a demonstaration of the ability to record information as a change in refractive-index using two-photon excitation, Figures 3(a) and 3(b) show the measured change in refractive-index produced at the focus spots. In recording an average power of 5 mW at the focus spot was used to record the information. A pattern (the letter C) consisting of 24 x 24 bits was recorded in the sample. The bit separation was 3.2μm, and the exposure time for each bit was 25 ms. In the reading process a laser beam of power less than 5mW was scanned across the sample to produce the DIC image. Figure 3(b) shows the deterioration of the recorded information after having been scanned 500 times. The contrast of the recorded bit in Figure 3(b) is 90% of that in Figure 3(a). This feature illustrates that there is a slight erasing of the information due to absorption of the light used for reading. The information recorded in Figure 3(c) used the same power and exposure time as used in Figure 3(a) and Figure 3(b). Figure 3(d) shows the same region as seen in Figure 3(c) after being exposed to the UV illumination for 1-2 seconds. The result shows the complete erasure of the previously recorded information.

Figure 4 demonstrates the ability of this system to record and read changes in refractive-index of multiple layers of information. Three layers of information were recorded with a layer separation of 10 μm. Each layer consists of a pattern of 24 x 24 bits. The first layer, recorded near the surface contains a pattern of the letter “A”. The second and third layers consist of the letters “B” and “C” respectively, thus the achieved 3D data density was approximately 10 Gbits/cm^3, which is comparable to that previously achieved in photochromic polymers, a photorefractive crystal and photobleaching materials.

Figure 5(a) shows the ability to record information as a change in refractive-index using continuous wave two-photon excitation. In recording an average power of 75 mW at the focus spot was used to record the information. A pattern (the letter E) consisting of 24 x 24 bits was recorded in the sample. The bit separation was 5.6 μm, and the exposure time for each bit was 2 ms. In the reading process a laser beam of power less than 5 mW was scanned across the sample to produce the DIC image. Figure 5(b) shows the same region as seen in Figure 5(a) after being exposed to the UV illumination for 1-2 seconds. The result shows the complete erasure of the previously recorded information. In Figure 5(c), a new pattern, the letter "F" is written into the same area as used in Figures 5(a) and 5(b). Two artifacts are marked with circles 1 and 2 in Figures 5(a), (b) and (c) showing that the same area was used to erase and rewrite information.

Figure 6 demonstrates the ability of this system to record and read changes in refractive-index of multiple layers of information. Three layers of information were recorded with a layer separation of 25 μm. Each layer consists of a pattern of 24 x 24 bits. The first layer, recorded near the surface contains a pattern of the letter “A”. The second and third layers consist of the letters “B” and “C”, respectively.

It will be seen from the above that the present invention provides an effective method of recording, reading, erasing and rewriting three dimensional data in relatively inexpensive photorefractive polymeric materials using either pulsed or continuous wave (CW) two-photon excitation to record and re-write

the data, and illuminating with radiation in the UV or visible region of the electromagnetic radiation to erase the recorded data.

– It will also be appreciated that various modifications, alterations and improvements may be made to the preferred embodiment described above without departing from the scope and spirit of the present invention. Such modifications or improvements that are envisaged to increase the storage capacity of the system include the following:

1. The compensation of small amounts of cross talk between the layers (see Figure 4) due to spherical aberration from the refractive-index mismatch between the recording material (n = 1.75) and the immersion medium (n = 1). The refractive-index mismatch results in an increase in the diffraction spot size at a deep position of a volume recording medium. As a result, a series of axial side peaks occur along the depth of the recording medium, thus resulting in cross talk between neighbouring data layers. It may be possible to overcome this problem thereby increasing the density of data by using a variable tube length method.

2. Instead of the Ti:sapphire laser operated in CW mode, other types of continuous wave (CW) laser beams may be used to produce the two-photon excitation. For example, with the help of a 1.2 W CW laser diode, operated at a near-infrared wavelength, a fast, low cost, compact, erasable two-photon 3D bit optical data storage system can be achieved.

3. Different photorefractive polymers may be used and the chemical properties of the materials may be modified to lead to an increase in the stability of the photorefractive polymer. By tailoring the absorption spectrum we can determine the wavelength of light that will affect the material. Creating a narrow absorption band in the UV or visible region will decrease the materials susceptibility to deterioration due to irradiation from the reading process or from incidental UV light (i.e. sunlight).

4. A method for increasing the density of the two-photon data storage system by utilising a recording method may be based on the polarisation state of the recording beam. This technique allows multiple bits to be recorded

at the same position within the material using different polarisation states of the recording beam, where upon reading, only the bits with an appropriate polarisation state are detected.

5. A method for selective bit erasure in the two-photon data storage system may be based on polarisation of the recording and reading beams. An individual bit can be selected and erased by changing the polarisation state of the recorded bit, so that it has an appropriate polarisation state which can either be detected or not detected upon reading.

CLAIMS

1. A method of writing and erasing optical data comprising:

– producing a beam of focusable, coherent light;

focussing the beam on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

2. A method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing a beam of coherent light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing another beam of coherent light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to re-write data in the photorefractive polymeric material.

3. A method according to claim 1 or claim 2 wherein the photorefractive material is illuminated with electro-magnetic radiation having a wavelength in the ultraviolet (UV) or visible spectrum to produce a redistribution of the spacial distribution of the electric charges forming bits of the data to erase the recorded data.

4. A method according to claim 3 wherein the photorefractive polymeric material is such that it absorbs radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum.

5. A method according to claim 3 or claim 4 wherein the maximum of the absorption band of the photorefractive polymeric material falls substantially within the range from about 380nm to about 600 nm.

6. A method according to any one of claims 3 to 5 wherein the photorefractive polymeric material is such that is absorbs substantially no radiation above a wavelength of about 630 nm.

7. A method according to any one the preceding claims wherein the data recorded in the photorefractive polymeric material is read by illuminating the photorefractive polymeric material with coherent light of a wavelength falling substantially within the range from about 630 nm to about 1200 nm.

8. A method according to any one of the preceding claims wherein the beam of focusable coherent light used to record data in the photorefractive material has a wavelength falling substantially within the range from about 750nm to about 1200 nm to cause two-photon excitation.

9. A method according to any one of the preceding claims wherein a pulsed laser beam is used to record data in the photorefractive polymeric material.

10. A method according to any one of claims 1 to 8 wherein a continuous wave laser beam is used to record data in the photorefractive polymeric material.

11. A method according to any one of the preceding claims wherein a polarised beam of focusable, coherent light is used to record polarised bits of data in the photorefractive polymeric material.

12. A method according to claim 11 wherein different polarisation states of the recording beam are used to record multiple bits of data at the same position having different polarisation states in the photorefractive polymeric material.

13. A method according to claim 11 or claim 12 wherein bits of recorded data are read by using a reading beam having an appropriate polarisation state.

14. A method according to any one of claims 11 to 13 wherein individual bits of data are erasable by changing the polarisation state of the individual bits.

15. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

16. A method according to any one of the preceding claims, wherein the photorefractive polymeric material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

17. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

18. A method according to any one of the preceding claims wherein the photorefractive polymeric material includs a plasticiser to reduce the glass transition temperature of the material.

19. A method according to any one of the preceding claims wherein the photorefractive material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive material:

25% - 100% of a polymer ;
0%-60% of a chromophore;
— 0%-5% of a photosensitive material; and
0% - 40% of a plasticiser.

20. A method according to claim 15 or claim 19 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

21. A method according to claim 15 or claim 19 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

22. A method according to claim 16 or any one of claims 19 to 21 wherein the chromophore comprises 2, 5- dimethyl – 4 – (p-nitro-phenylazo) anisole (DMNPAA).

23. A method according to claim 17 or any one of claims 19 to 22 wherein the photosensitive material comprises 2, 4, 7-trinitro-9-fluorenone (TNF).

24. A method according to any one of claims 19 to 23 wherein the plasticizer comprises *N*-ethylcarbazole (ECZ).

25. A photorefractive polymeric material for use in a method of erasable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the phtotrefractive material is such as to enable the recording of bits of data by two photon exciation, the reading of the bits of data by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band.

26. A photorefractive polymeric material according to claim 25 wherein the maximum of the absorption band of the photorefractive material falls substantially within the range from about 380 nm to about 600 nm.

27. A photorefractive polymeric material according to claim 25 or claim 26 wherein the upper end of the absorption band of the photorefractive polymeric material is about 630 nm.

28. A photorefractive polymeric material according to any one of claims 25 to 27 wherein the material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

29. A photorefractive polymeric material according to any one of claims 25 to 28 wherein the material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

30. A photorefractive polymeric material according to claim 29 wherein the chromophore is present by an amount falling substantially within the range from about 0.5% to about 60% by percentage weight of the total weight of the material.

31. A photorefractive polymeric material according to any one of claims 25 to 30 wherein the material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

32. A photorefractive polymeric material according to claim 31 wherein the photosensitive material is present by an amount falling substantially within the range from about 0.5% to about 5% by percentage weight of the total weight of the photosensitive material.

33. A photorefractive polymeric material according to any one of claims 25 to 32 wherein the material includes a plasticiser to reduce the glass transition temperature of the material.

34. A photorefractive polymeric material according to claim 33 wherein the plasticizer is present by an amount falling substantially within the range from 0% to about 40% by percentage weight of the total weight of the photorefractive polymeric material.

35. A photorefractive polymeric material for use in a method of optical data storage, wherein the material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material;

25% - 99.5% of a polymer;
0% - 60% of a chromophore;
0% - 5% of a photosensitive material; and
0% - 40% of a plasticiser.

36. A photorefractive polymeric material according to claim 28 or claim 35 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

37. A photorefractive polymeric material according to claim 28 or claim 35 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

38. A photorefractive polymeric material according to any one of claims 29, 30 or 35 to 37 wherein the chromophore comprises 2,5-dimethyl-4-(p-nitro phenylazo) anisole (DMNPAA).

39. A photorefractive polymeric material according to any one of claims 31, 32, or 35 to 38 wherein the photosensitive material comprises 2, 4, 7-trinitro–9-fluorenone (TNF).

40. A photorefractive polymeric material according to any one of claims 33 to 39 wherein the plasticiser comprises *N*-ethylcarbazole (ECZ).

41. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly(*N*-vinylcarbazole) (PVK);
2,5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA)
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

42. A photorefractive material according to claim 41 wherein the PVK;DMNPAA;TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive material 33:50:1:16.

43. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly (methyl methacrylate) (PMMA);
2, 5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA);
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

44. A photorefractive polymeric material according to claim 43 wherein the PMMA: DMNPAA; TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive polymeric material 73:10:1:16

AMENDED CLAIMS

[received by the International Bureau on 23 June 2000 (23.06.00); original claims 1 – 44 replaced by new claims 1 – 45 (8 pages)]

1. A method of writing and erasing optical data comprising:

– focussing light on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

2. A method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to re-write data in the photorefractive polymeric material.

3. A method according to claim 1 or claim 2 wherein the modulation of the refractive index caused by the two-photon excitation is a refractive index inhomogeneity resulting from a non-uniform space-charge distribution within the region of excitation within the photorefractive polymeric material.

4. A method according to any one of claims 1 to 3 wherein the photorefractive material is illuminated with electro-magnetic radiation having a wavelength in the ultraviolet (UV) or visible spectrum to produce a redistribution of the spacial distribution of the electric charges forming bits of the data to erase the recorded data.

5. A method according to claim 4 wherein the photorefractive polymeric material is such that it absorbs radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum.

6. A method according to claim 4 or claim 5 wherein the maximum of the absorption band of the photorefractive polymeric material falls substantially within the range from about 380nm to about 600 nm.

7. A method according to any one of claims 4 to 6 wherein the photorefractive polymeric material is such that is absorbs substantially no radiation above a wavelength of about 630 nm.

8. A method according to any one the preceding claims wherein the data recorded in the photorefractive polymeric material is read by illuminating the photorefractive polymeric material with coherent light of a wavelength falling substantially within the range from about 630 nm to about 1200 nm.

9. A method according to any one of the preceding claims wherein the light used to record data in the photorefractive material has a wavelength falling substantially within the range from about 750nm to about 1200 nm to cause two-photon excitation.

10. A method according to any one of the preceding claims wherein a pulsed laser beam is used to record data in the photorefractive polymeric material.

11. A method according to any one of claims 1 to 9 wherein a continuous wave laser beam is used to record data in the photorefractive polymeric material.

12. A method according to any one of the preceding claims wherein polarised coherent light is used to record polarised bits of data in the photorefractive polymeric material.

13. A method according to claim 12 wherein different polarisation states of the recording beam are used to record multiple bits of data at the same position having different polarisation states in the photorefractive polymeric material.

14. A method according to claim 12 or claim 13 wherein bits of recorded data are read by using a reading beam having an appropriate polarisation state.

15. A method according to any one of claims 12 to 14 wherein individual bits of data are erasable by changing the polarisation state of the individual bits.

16. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

17. A method according to any one of the preceding claims, wherein the photorefractive polymeric material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

18. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

19. A method according to any one of the preceding claims wherein the photorefractive polymeric material includs a plasticiser to reduce the glass transition temperature of the material.

20. A method according to any one of the preceding claims wherein the photorefractive material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive material:

25% - 100% of a polymer ;
0%-60% of a chromophore;
0%-5% of a photosensitive material; and
0% - 40% of a plasticiser.

21. A method according to claim 16 or claim 20 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

22. A method according to claim 16 or claim 20 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

23. A method according to claim 17 or any one of claims 20 to 22 wherein the chromophore comprises 2, 5- dimethyl – 4 – (p-nitro-phenylazo) anisole (DMNPAA).

24. A method according to claim 18 or any one of claims 20 to 22 wherein the photosensitive material comprises 2, 4, 7-trinitro-9-fluorenone (TNF).

25. A method according to any one of claims 20 to 24 wherein the plasticizer comprises *N*-ethylcarbazole (ECZ).

26. A photorefractive polymeric material for use in a method of erasable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the phtotrefractive material is such as to enable the recording of bits of data by two photon exciation, the reading of the bits of data

by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band.

27. A photorefractive polymeric material according to claim 26 wherein the maximum of the absorption band of the photorefractive material falls substantially within the range from about 380 nm to about 600 nm.

28. A photorefractive polymeric material according to claim 26 or claim 27 wherein the upper end of the absorption band of the photorefractive polymeric material is about 630 nm.

29. A photorefractive polymeric material according to any one of claims 26 to 28 wherein the material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

30. A photorefractive polymeric material according to any one of claims 26 to 29 wherein the material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

31. A photorefractive polymeric material according to claim 30 wherein the chromophore is present by an amount falling substantially within the range from about 0.5% to about 60% by percentage weight of the total weight of the material.

32. A photorefractive polymeric material according to any one of claims 26 to 31 wherein the material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

33. A photorefractive polymeric material according to claim 32 wherein the photosensitive material is present by an amount falling substantially within the

range from about 0.5% to about 5% by percentage weight of the total weight of the photosensitive material.

34. A photorefractive polymeric material according to any one of claims 26 to 33 wherein the material includes a plasticiser to reduce the glass transition temperature of the material.

35. A photorefractive polymeric material according to claim 33 wherein the plasticizer is present by an amount falling substantially within the range from 0% to about 40% by percentage weight of the total weight of the photorefractive polymeric material.

36. A photorefractive polymeric material for use in a method of erasable/rewritable optical data storage, wherein the material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material;

25% - 100% of a polymer;
0% - 60% of a chromophore;
0% - 5% of a photosensitive material; and
0% - 40% of a plasticiser.

37. A photorefractive polymeric material according to claim 29 or claim 36 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

38. A photorefractive polymeric material according to claim 29 or claim 36 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

39. A photorefractive polymeric material according to any one of claims 30, 31 or 36 to 38 wherein the chromophore comprises 2,5-dimethyl-4-(p-nitro phenylazo) anisole (DMNPAA).

40. A photorefractive polymeric material according to any one of claims 32, 34 or 36 to 39 wherein the photosensitive material comprises 2, 4, 7-trinitro–9-fluorenone (TNF).

41. A photorefractive polymeric material according to any one of claims 34 to 40 wherein the plasticiser comprises *N*-ethylcarbazole (ECZ).

42. A photorefractive polymeric material for use in a method of erasable/rewritable optical data storage comprising the following materials:

poly(*N*-vinylcarbazole) (PVK);
2,5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA)
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

43. A photorefractive material according to claim 42 wherein the PVK;DMNPAA;TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive material 33:50:1:16.

44. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly (methyl methacrylate) (PMMA);
2, 5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA);
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

45. A photorefractive polymeric material according to claim 44 wherein the PMMA: DMNPAA; TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive polymeric material 73:10:1:16.

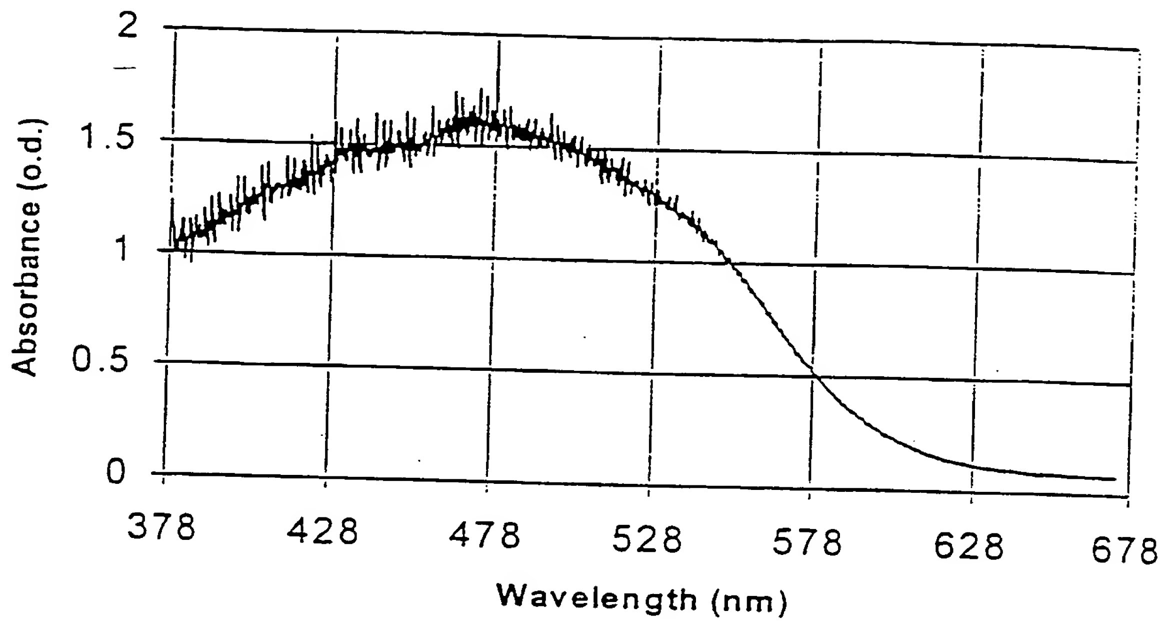

2
1.5
1
0.5
0
Absorbance (o.d.)
378
428
478
528
578
628
678
Wavelength (nm)

Figure 1.

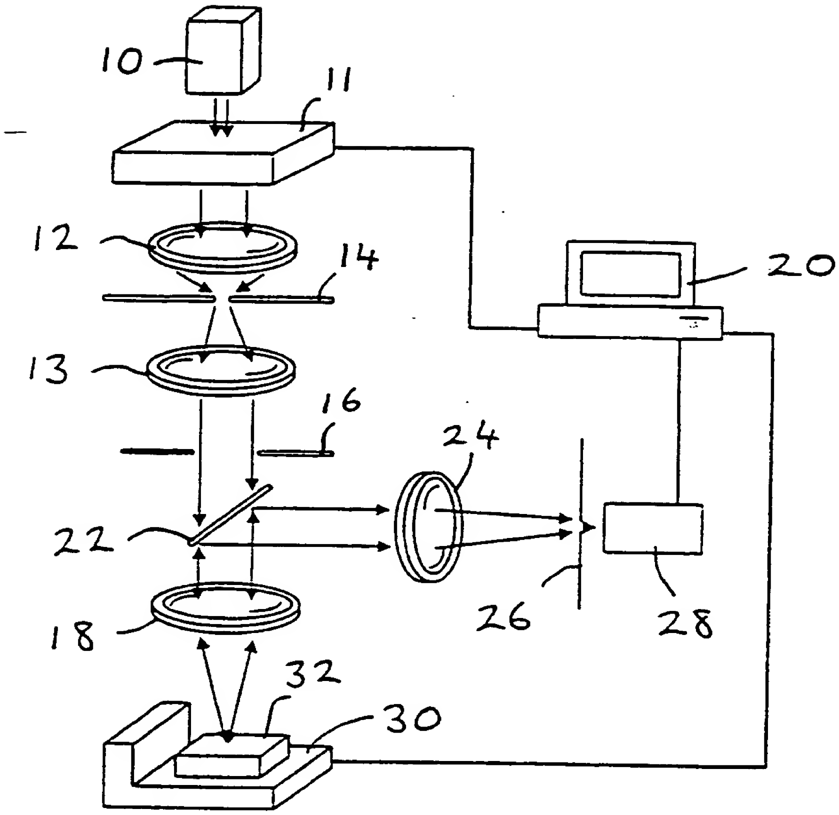
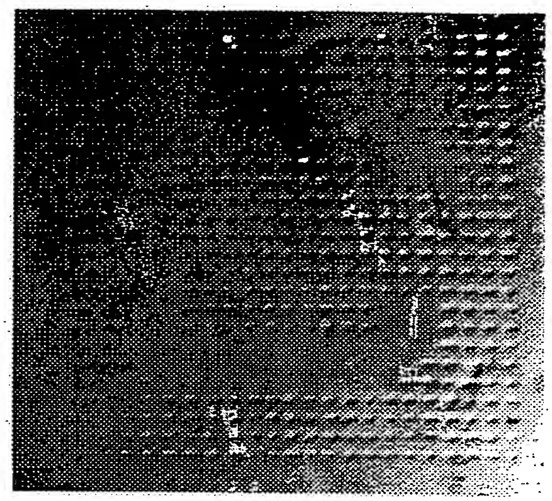
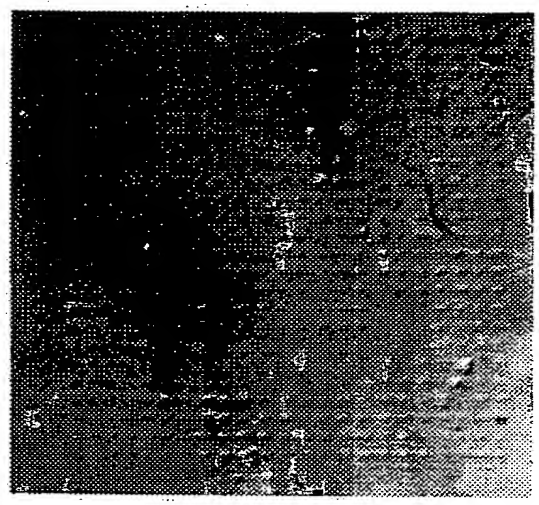


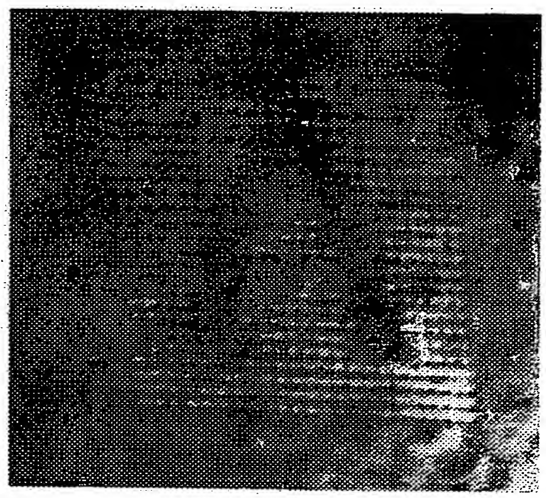
Figure 2.



(a)



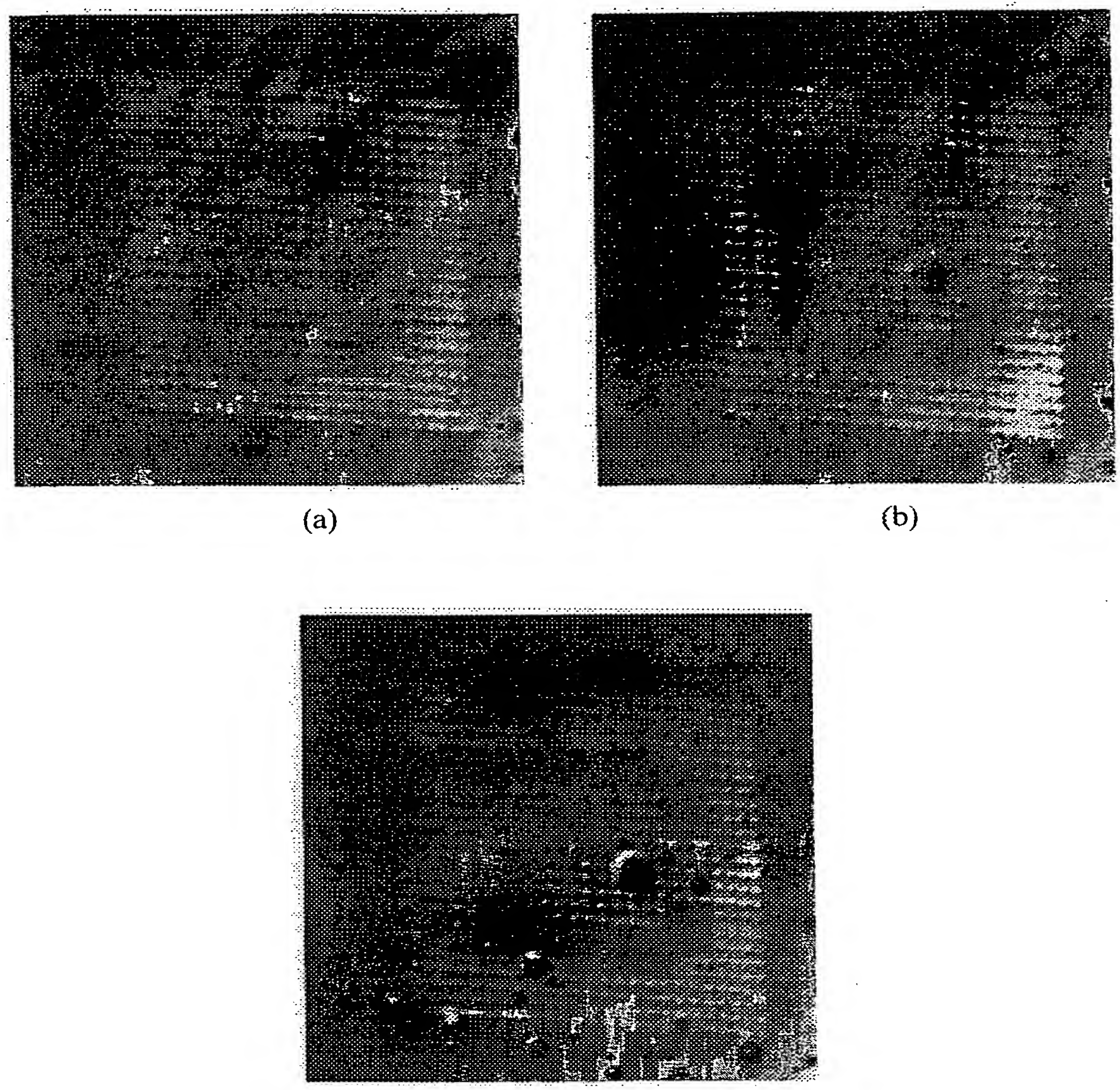
(b)



(c)

(d)

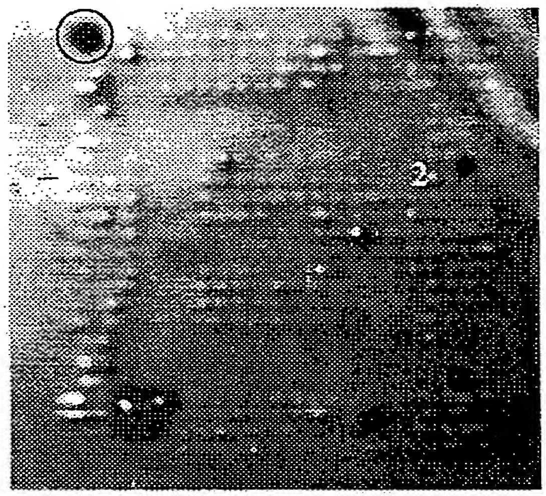
Figure 3.



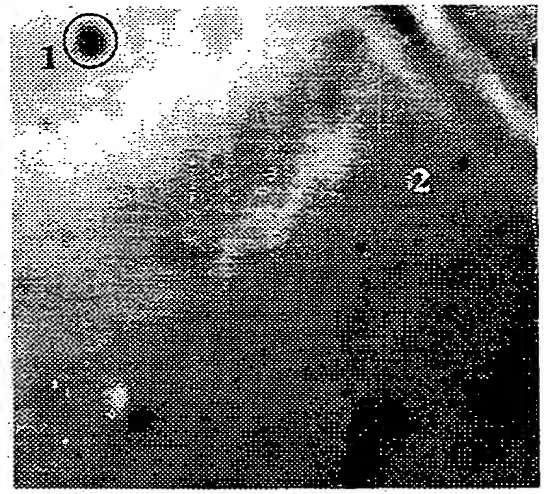
(a) (b)

(c)

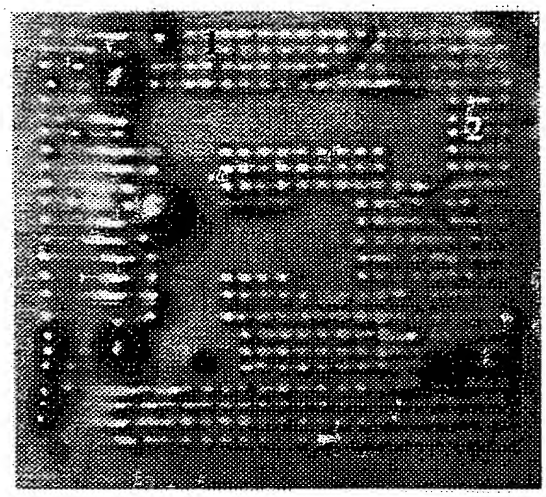
Figure 4.



(a)

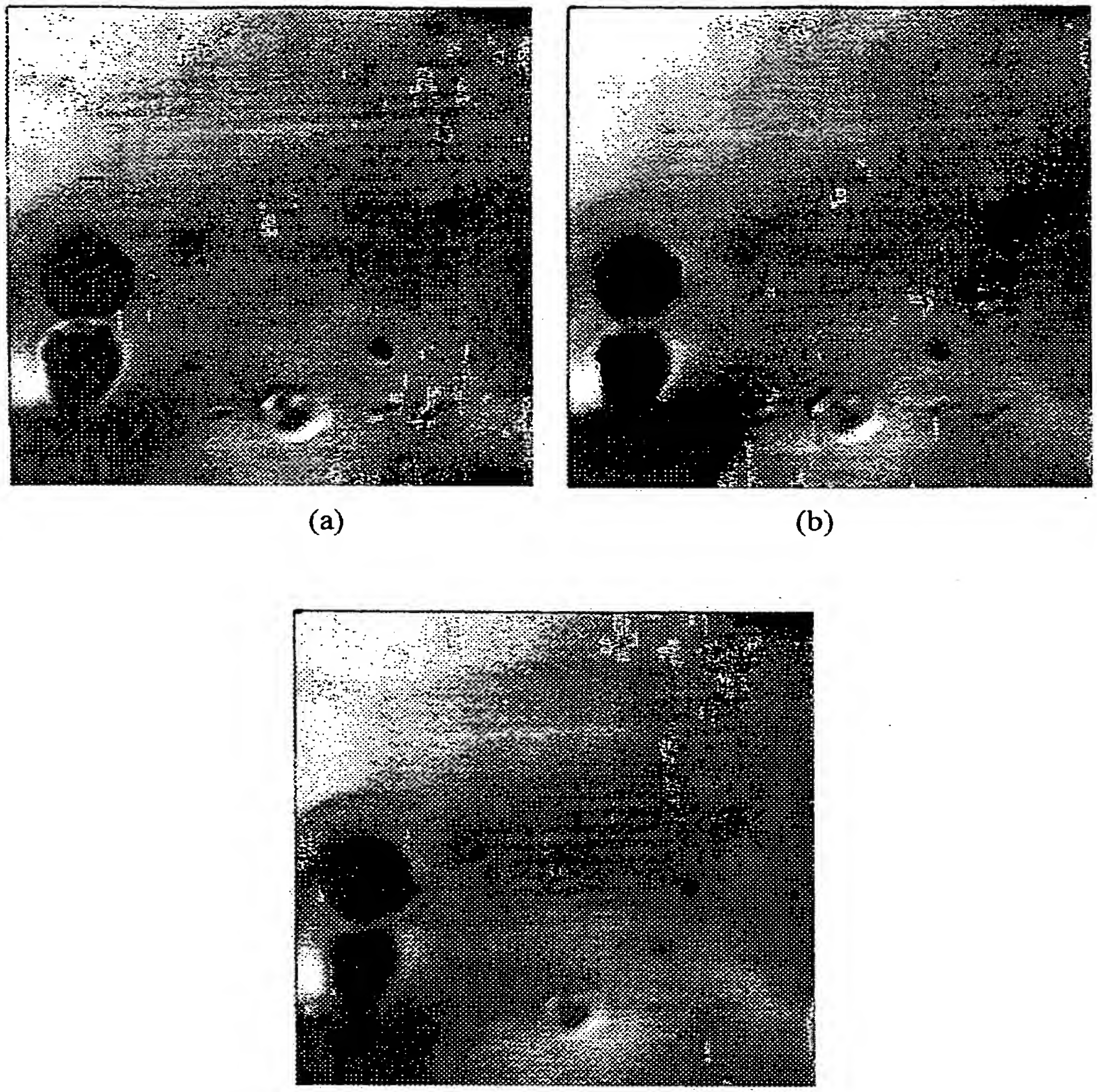


(b)



(c)

Figure 5.



(a) (b)

(c)

Figure 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00117

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ^{7}: G11B 7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT, INTERNET, USPTO
keywords: two photon excitation, polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5472759 (CHEN et al.) 5 December 1995	1 to 17, 25 to 29, and 31
X	US 5289407 (STRICKLER et al.) 22 February 1994	1 to 17, 25 to 29, and 31
X	US 5268862 (RENTZEPIS) 7 December 1993	1 to 17, 25 to 29, and 31

[X] Further documents are listed in the continuation of Box C [ ] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 9 March 2000	Date of mailing of the international search report 15 MAR 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **P. CLAYTON-STAMM** Telephone No : (02) 6283 2168

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00117

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9302454 (CORNELL RESEARCH FOUNDATION INC.) 4 February 1993	1 to 17, 25 to 29, and 31

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00117

Box I **Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos : 35

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   Claim 35 is speculative and includes within its scope a polymer.

3. ☐ Claims Nos :

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 35, 41, 43 and 44 (and the claims appended to them) define polymer compositions for optical discs. Claim 1 defines a method for writing and erasing optical data using two photon excitation. This feature, at least, is absent from the above mentioned claims.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

   1 to 34, 36 to 40, and 42.

Remark n Protest ☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FREEHILLS
CARTER
SMITH &
BEADLE

23 June 2000

International Bureau of WIPO
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1211 Geneva 20
Switzerland

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No. of Pages:
Fee Earner's Pin: 40545
Ext. (Sec): 1103

Writer's Direct No: 9288 1136
Writer's Email: roger_green@freehills.com.au

Dear Sirs,

RE: International Patent Application No. PCT/AU00/00117
in the name of Victoria University of Technology
Our Ref: 40351976 (formerly #30008) ROG JA

We refer to the Supplementary International Search Report dated 26 April 2000 on this application and lodge herewith substitute pages 13 to 20 to replace the corresponding pages 13 to 19 of the claims presently on file in this application. In the substitute pages of the claims lodged herewith, claims 1 and 2 have been amended, a new dependent claim 3 has been added, the wording of newly numbered claims 9, 12, 36 and 42 corresponding to previous claims 8, 11, 35 and 41 have been amended, and the remaining claims and their dependencies have also been amended owing to the addition of new claim 3.

We request that the amended claims filed herewith be published with the International application when it is published Internationally.

We also advise that the address of one of the inventors, Min Gu has changed to 4 Maverick Close, Doncaster, Victoria 3108, Australia. Furthermore, we ask you to note that the name and address of our firm has changed from Carter Smith & Beadle to Freehills, Carter Smith & Beadle of 101 Collins Street, Melbourne, Victoria 3000, Australia. We request that these changes also be published when the International application is published.

Finally, please note our new contact details and our new reference number for this matter which should be used in future correspondence in connection with this application.

Yours sincerely
FREEHILLS CARTER SMITH & BEADLE

J Roger Green
Enc*

c.c. International Searching Authority
Australian Patent Office
Woden A.C.T.

CLAIMS

1. A method of writing and erasing optical data comprising:

focussing light on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

2. A method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to re-write data in the photorefractive polymeric material.

3. A method according to claim 1 or claim 2 wherein the modulation of the refractive index caused by the two-photon excitation is a refractive index inhomogeneity resulting from a non-uniform space-charge distribution within the region of excitation within the photorefractive polymeric material.

4. A method according to any one of claims 1 to 3 wherein the photorefractive material is illuminated with electro-magnetic radiation having a wavelength in the ultraviolet (UV) or visible spectrum to produce a redistribution of the spacial distribution of the electric charges forming bits of the data to erase the recorded data.

5. A method according to claim 4 wherein the photorefractive polymeric material is such that it absorbs radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum.

6. A method according to claim 4 or claim 5 wherein the maximum of the absorption band of the photorefractive polymeric material falls substantially within the range from about 380nm to about 600 nm.

7. A method according to any one of claims 4 to 6 wherein the photorefractive polymeric material is such that is absorbs substantially no radiation above a wavelength of about 630 nm.

8. A method according to any one the preceding claims wherein the data recorded in the photorefractive polymeric material is read by illuminating the photorefractive polymeric material with coherent light of a wavelength falling substantially within the range from about 630 nm to about 1200 nm.

9. A method according to any one of the preceding claims wherein the light used to record data in the photorefractive material has a wavelength falling substantially within the range from about 750nm to about 1200 nm to cause two-photon excitation.

10. A method according to any one of the preceding claims wherein a pulsed laser beam is used to record data in the photorefractive polymeric material.

11. A method according to any one of claims 1 to 9 wherein a continuous wave laser beam is used to record data in the photorefractive polymeric material.

12. A method according to any one of the preceding claims wherein polarised coherent light is used to record polarised bits of data in the photorefractive polymeric material.

13. A method according to claim 12 wherein different polarisation states of the recording beam are used to record multiple bits of data at the same position having different polarisation states in the photorefractive polymeric material.

14. A method according to claim 12 or claim 13 wherein bits of recorded data are read by using a reading beam having an appropriate polarisation state.

15. A method according to any one of claims 12 to 14 wherein individual bits of data are erasable by changing the polarisation state of the individual bits.

16. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

17. A method according to any one of the preceding claims, wherein the photorefractive polymeric material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

18. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

19. A method according to any one of the preceding claims wherein the photorefractive polymeric material includs a plasticiser to reduce the glass transition temperature of the material.

20. A method according to any one of the preceding claims wherein the photorefractive material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive material:

25% - 100% of a polymer ;
0%-60% of a chromophore;
0%-5% of a photosensitive material; and
0% - 40% of a plasticiser.

21. A method according to claim 16 or claim 20 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

22. A method according to claim 16 or claim 20 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

23. A method according to claim 17 or any one of claims 20 to 22 wherein the chromophore comprises 2, 5- dimethyl – 4 – (p-nitro-phenylazo) anisole (DMNPAA).

24. A method according to claim 18 or any one of claims 20 to 22 wherein the photosensitive material comprises 2, 4, 7-trinitro-9-fluorenone (TNF).

25. A method according to any one of claims 20 to 24 wherein the plasticizer comprises *N*-ethylcarbazole (ECZ).

26. A photorefractive polymeric material for use in a method of erasable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the phtotrefractive material is such as to enable the recording of bits of data by two photon exciation, the reading of the bits of data

by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band.

27. A photorefractive polymeric material according to claim 26 wherein the maximum of the absorption band of the photorefractive material falls substantially within the range from about 380 nm to about 600 nm.

28. A photorefractive polymeric material according to claim 26 or claim 27 wherein the upper end of the absorption band of the photorefractive polymeric material is about 630 nm.

29. A photorefractive polymeric material according to any one of claims 26 to 28 wherein the material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

30. A photorefractive polymeric material according to any one of claims 26 to 29 wherein the material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

31. A photorefractive polymeric material according to claim 30 wherein the chromophore is present by an amount falling substantially within the range from about 0.5% to about 60% by percentage weight of the total weight of the material.

32. A photorefractive polymeric material according to any one of claims 26 to 31 wherein the material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

33. A photorefractive polymeric material according to claim 32 wherein the photosensitive material is present by an amount falling substantially within the

range from about 0.5% to about 5% by percentage weight of the total weight of the photosensitive material.

34. A photorefractive polymeric material according to any one of claims 26 to 33 wherein the material includes a plasticiser to reduce the glass transition temperature of the material.

35. A photorefractive polymeric material according to claim 33 wherein the plasticizer is present by an amount falling substantially within the range from 0% to about 40% by percentage weight of the total weight of the photorefractive polymeric material.

36. A photorefractive polymeric material for use in a method of erasable/rewritable optical data storage, wherein the material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material;

25% - 100% of a polymer;
0% - 60% of a chromophore;
0% - 5% of a photosensitive material; and
0% - 40% of a plasticiser.

37. A photorefractive polymeric material according to claim 29 or claim 36 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

38. A photorefractive polymeric material according to claim 29 or claim 36 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

39. A photorefractive polymeric material according to any one of claims 30, 31 or 36 to 38 wherein the chromophore comprises 2,5-dimethyl-4-(p-nitro phenylazo) anisole (DMNPAA).

40. A photorefractive polymeric material according to any one of claims 32, 34 or 36 to 39 wherein the photosensitive material comprises 2, 4, 7-trinitro–9-fluorenone (TNF).

41. A photorefractive polymeric material according to any one of claims 34 to 40 wherein the plasticiser comprises *N*-ethylcarbazole (ECZ).

42. A photorefractive polymeric material for use in a method of erasable/rewritable optical data storage comprising the following materials:

poly(*N*-vinylcarbazole) (PVK);
2,5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA)
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

43. A photorefractive material according to claim 42 wherein the PVK;DMNPAA;TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive material 33:50:1:16.

44. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly (methyl methacrylate) (PMMA);
2, 5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA);
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

45. A photorefractive polymeric material according to claim 44 wherein the PMMA: DMNPAA; TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive polymeric material 73:10:1:16.

24 November 2000

International Preliminary Examining Authority
Australian Patent Office

Sir,

RE: International Patent Application No. PCT/AU00/00117
in the name of Victoria University of Technology
Our Ref: 40351976 ROG JA

We refer to the Written Opinion dated 25 September 2000.

* We lodge herewith substitute page 5 and 16 to 20 to replace the corresponding pages presently on file. For the Examiner's convenience, we also enclose copies of those pages showing the amendments in manuscript.

We note that claims 1-18, 20, 26-30, 32, 35-44 are considered by the Examiner to lack novelty and an inventive step and we submit the following observations in response to the Examiner's opinion.

The present invention as claimed in claim 1 involves a method of writing and erasing optical data comprising the steps of

(a) focussing light on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index of the material at the focal point to record data; and

(b) illuminating the material with radiation to erase the recorded data.

The method of independent claim 2 includes the further step of re-writing data using focussed light to produce a photo-refractive effect.

It is respectfully submitted that the present invention is clearly novel because none of the cited references discloses a method of optical data storage which is erasable or rewritable and which includes all of the features of claims 1 and 2 as will be apparent from the following discussion of the cited references.

101 Collins Street Melbourne Victoria 3000 Australia
Telephone (03) 9288 1577 Int+ (61 3) 9288 1577 Facsimile (03) 9288 1567
DX 240 Melbourne

U.S. 5,472,759 (Chen et al)

This patent discloses optical memory materials for two-photon data storage, but the materials described in this patent are photochromic materials, in contrast to the photorefractive polymeric materials in the present invention in which the refractive index of the material at the focal point of the focussed beam is modulated. This is apparent from column 3, lines 7 to 11 which recite the memory material includes a mixture of a frequency up-conversion material such as an "up-conversion" dye, a photochromic storage material, and a flurorescent material such as a "signal dye" which responds to the local state of the adjacent photochromic material. Also, the particular examples of storage materials disclosed and claimed in U.S. 5,472,759 are photochromic fulgide compounds. Further, the optical data storage materials described require a method of single photon fluorescence for reading the recorded bits which is not used in the present invention.

U.S. 5,289,407 and its equivalent WO 93/02454 (Strickler et al)

These prior specifications disclose a permanent method for three-dimensional optical data storage and retrieval which is not erasable and re-writable. The specific method disclosed involves a modification of the density of the photosensitive material which arises from the polymerisation in the focal region of a photopolymerisable solution to produce a bead of material which is different from the surrounding material at the focal point. This is a permanent, irreversible change to the photosensitive material, in contrast to the present invention which involves modulation of the refractive index at the focal point to record data which can be reversed by illuminating the material with radiation to erase the recorded data. This different is further apparent from claim 3 of the present application which recites that "the modulation of the refractive index caused by two-photon excitation is a refractive index inhomogeneity resulting from a non-uniform space-charge distrubution within the region of excitation within the photorefractive material. There is no disclosure or suggestion by Strickler et al of a method of optical data storage involving modulation of the refractive index of a photorefractive polymeric material which is erasable and rewritable and so it is submitted that claims 1 and 2 are clearly novel and inventive having regard to Strickler et al.

U.S. 5,268,862 (Rentzepis)

This patent discloses the use of a photochromic material, specifically spirobenzopyran, embedded in a polymer matrix as a three-dimensional memory. Upon excitation by two intersecting radiation beams the photochromic medium at the point of intersection changes to a second isomeric form thereby forming the bit of data which is read by fluorescence. This is quite different from the present invention which records data by focussing a beam of light on a photo-refractive polymeric material to modulate the refractive index at the focal point by two-photon excitation.

In view of the observations above, it is respectfully submitted that the present invention as claimed in claims 1 and 2 is clearly novel and inventive over U.S. 5,268,862, U.S. 5,472,759 and U.S. 5,289,407. Further, dependent claims 3 to 25 are also novel and inventive insofar as they are appended to claim 1 or claim 2.

It is also submitted that independent claim 26 and claims dependent thereon, which claim a photorefractive polymeric material adapted for use in a method of erasable data storage, is clearly novel over U.S. 5,472,757 (Chen) and U.S. 5,268,862 (Rentzepis), both of which disclose

photochromic materials rather than the photorefractive materials of the present invention, and over U.S. 5,289,407 (Strickler) which does not disclose a photorefractive material having an absorption band which is such as to enable erasing of bits of data by illumination with radiation outside the absorption band that allows the recording of bits of data by two photo excitation.

With regard to claims 35 to 44 which are directed to compositions of photorefractive materials for use in the present invention, we wish to make the following submissions in response to the Examiner's comment that U.S. 5,744,267 and U.S. 5,724,460 disclose photorefractive polymers having all the features of these claims.

U.S 5,744,267 (Meerholz et al)

We note that this patent relates to a photorefractive polymer for holographic testing and image processing and a holographic device made from such a polymer. Holographic devices, by design, require the interference from two non-focused intersecting beams. As a result of the weak interaction with the material, a poling field produced from two transparent electrodes is required. Neither of these are used or required in the present invention.

In contrast to U.S. 5,744,267, amended claims 35 and 42 and directed to a photorefractive optical data storage medium adapted for use in a method of erasable/rewritable optical data storage in which light is focussed on the data storage medium to modulate the refractive index at the focal point by two-photon excitation.

As U.S. 5,744,267 does not disclose or suggest a photorefractive material adapted for use in such a method, it is submitted that the present invention as claimed in claims 35 to 43 is novel and inventive having regard to U.S. 5,744,267.

U.S. 5,724,460 (Hayden et al)

This patent relates to a photorefractive thin film polymer waveguide in which a change in the refractive index is produced by two intersecting beams, with the assistance of a poling electric field generated by applying a voltage across two indium tin oxide (ITO) plates. This disclosure is not at all relevant to a photorefractive optical data storage medium, let alone such a medium specifically adapted for a method of erasable/rewritable data storage in which a focussed beam is used to record bits of data by two-photon excitation. It is therefore submitted that claims 35 to 43 are clearly novel and inventive having regard to US 5,724,460.

With regard to dependent claim 38 and independent claim 44, neither US 5,744,267 nor US 5,724,460 discloses a photorefractive polymeric material for use in a method of optical data storage which includes poly (methyl methacrylate), PMMA, and so it is respectfully submitted that claims 38 and 44 are clearly novel and inventive having regard to US 5,744,267 and US 5,724,460.

In summary, the Applicant is the first to have developed a method of optical data storage using two-photon excitation of photo-refractive polymers which is both erasable and re-writable, as opposed to US 5,289,407 (Strickler) which only discloses a permanent method for optical data storage using a photopolymerisable solution. Further, the Applicant achieves this by inducing a refractive index inhomogeneity resulting from a non-uniform space-charge distribution in the region of excitation within the photorefractive polymeric material.

The use of photorefractive polymers has several advantages over photochromic materials such as disclosed in U.S. 5,472,759 (Chen) and U.S. 5,268,862 (Rentzepis) in that photorefractive polymers are relatively inexpensive to produce as opposed to photochromic materials, such as spirobezopyran, that undergo a change in isomer states under two-photon excitation. This opens up the possibility of utilising the method and photo-refractive polymers of the present invention for effective three-dimensional erasable/rewritable optical data storage on a commercial basis.

Furthermore, the use of the photorefractive polymeric materials as claimed in claims 26 to 44 as erasable/rewritable optical data storage media in which the refractive index is modulated at the focal point has not been previously proposed. Thus those claims are distinguished from US 5,744,267 (Meerholtz) which discloses photorefractive polymer composites for holographic testing and image processing which is quite a different process, and from US 5,724,460 (Hayden) which does not even relate to optical data storage.

In view of the above, it is submitted that the present invention as claimed in all of the claims is not only novel, but also clearly inventive having regard to the cited reference.

We therefore look forward to receiving a favourable International Preliminary Examination Report on this application at an early date.

Yours respectfully
Freehills Carter Smith Beadle

J Roger Green
Enc*

25% - 99.5% of a polymer, such as PVK or PMMA;

0.5% - 60% of a chromophore, such as DMNPAA;

0.5%- 5% of a photosensitive material, such as TNF; and

0% - 40% of a plasticiser, such as ECZ.

Preferred embodiments of the present invention using cheap photorefractive polymers as recording materials for rewritable/erasable 3D bit optical data storage under two-photon excitation to produce a high-density 3D optical data storage system will now be described by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the absorption curve of a photorefractive polymeric material for use in the present invention;

Figure 2 is a schematic diagram of a two-photon excitation microscope used to record data bits in a photorefractive polymer;

Figure 3(a) is a 24 x 24 bit pattern of the letter "C" recorded by two-photon excitation in a photorefractive polymer PVK upon its first reading;

Figure 3(b) is the same region after reading 500 times;

Figure 3(c) is a 24 x 24 bit pattern of the letter "A";

Figure 3(d) is the same region as Figure 3(c) after being exposed to UV illumination showing complete erasure of the recorded information;

Figure 4 shows recorded 24 x 24 bit patterns at different depths in the photorefractive polymer PVK using two-photon excitation;

Figure 4(a) shows a first layer including letter "A";

Figure 4(b) shows a second layer including letter "B" and

Figure 4(c) shows a third layer including letter "C";

Figure 5 (a) is a bit pattern of the letter "E" recorded by two-photon excitation in another photorefractive polymer (PMMA).

Figure 5 (b) is the same region as Figure 5(a) after being exposed to UV illumination showing erasure of the recorded information;

Figure 5(c) is a bit pattern of the letter "F" written into the same area as Figures 1 and 2;

20. A method according to any one of the preceding claims wherein the photorefractive material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive material:

25% - 99.5% of a polymer ;
0.5%-60% of a chromophore;
0.5%-5% of a photosensitive material; and
0% - 40% of a plasticiser.

21. A method according to claim 16 or claim 20 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

22. A method according to claim 16 or claim 20 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

23. A method according to claim 17 or any one of claims 20 to 22 wherein the chromophore comprises 2, 5- dimethyl – 4 – (p-nitro-phenylazo) anisole (DMNPAA).

24. A method according to claim 18 or any one of claims 20 to 22 wherein the photosensitive material comprises 2, 4, 7-trinitro-9-fluorenone (TNF).

25. A method according to any one of claims 20 to 24 wherein the plasticizer comprises *N*-ethylcarbazole (ECZ).

26. A photorefractive polymeric optical data storage material for use in a method of erasable/rewritable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the photorefractive material is such as to enable the recording of bits of data by two photon

excitation, the reading of the bits of data by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band.

27. A photorefractive polymeric material according to claim 26 wherein the maximum of the absorption band of the photorefractive material falls substantially within the range from about 380 nm to about 600 nm.

28. A photorefractive polymeric material according to claim 26 or claim 27 wherein the upper end of the absorption band of the photorefractive polymeric material is about 630 nm.

29. A photorefractive polymeric material according to any one of claims 26 to 28 wherein the material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

30. A photorefractive polymeric material according to any one of claims 26 to 29 wherein the material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

31. A photorefractive polymeric material according to claim 30 wherein the chromophore is present by an amount falling substantially within the range from about 0.5% to about 60% by percentage weight of the total weight of the material.

32. A photorefractive polymeric material according to any one of claims 26 to 31 wherein the material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

33. A photorefractive polymeric material according to claim 32 wherein the photosensitive material is present by an amount falling substantially within the

range from about 0.5% to about 5% by percentage weight of the total weight of the photosensitive material.

34. A photorefractive polymeric material according to any one of claims 26 to 33 wherein the material includes a plasticiser to reduce the glass transition temperature of the material.

35. A photorefractive polymeric material according to claim 33 wherein the plasticizer is present by an amount falling substantially within the range from 0% to about 40% by percentage weight of the total weight of the photorefractive polymeric material.

36. A photorefractive optical data storage medium for use in a method of erasable/rewritable optical data storage in which light is focussed on the data storage medium to modulate the refractive index at the focal point by two-photon excitation, wherein the medium includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive data storage medium.

25% - 99.5% of a polymer;
0.5% - 60% of a chromophore;
0.5% - 5% of a photosensitive material; and
0% - 40% of a plasticiser.

37. A photorefractive optical data storage medium according to claim 29 or claim 36 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

38. A photorefractive optical data storage medium according to claim 29 or claim 36 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

39. A photorefractive optical data storage medium according to any one of claims 30, 31 or 36 to 38 wherein the chromophore comprises 2,5-dimethyl-4-(p-nitro phenylazo) anisole (DMNPAA).

40. A photorefractive optical data storage medium according to any one of claims 32, 34 or 36 to 39 wherein the photosensitive material comprises 2, 4, 7-trinitro–9-fluorenone (TNF).

41. A photorefractive optical data storage medium according to any one of claims 34 to 40 wherein the plasticiser comprises *N*-ethylcarbazole (ECZ).

42. A photorefractive optical data storage medium adapted for use in a method of erasable/rewritable optical data storage in which light is focused on the data storage medium to modulate the refractive index at the focal point by two photon excitation, wherein the medium includes the following materials:

poly(*N*-vinylcarbazole) (PVK);
2,5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA)
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

43. A photorefractive optical data storage medium according to claim 42 wherein the PVK;DMNPAA;TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive material 33:50:1:16.

44. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly (methyl methacrylate) (PMMA);
2, 5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA);
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

45. A photorefractive polymeric material according to claim 44 wherein the PMMA: DMNPAA; TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive polymeric material 73:10:1:16.

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:	PCT
FREEHILLS CARTER SMITH & BEADLE Level 47 101 Collins Street MELBOURNE VIC 3000	WRITTEN OPINION (PCT Rule 66)
	Date of mailing (*day/month/year*) 25 September 2000
Applicant's or agent's file reference #30008 JRG	**REPLY DUE** within **TWO MONTHS** from the above date of mailing

International application No.	International filing date (*day/month/year*)	Priority Date (*day/month/year*)
PCT/AU00/00117	16 February 2000	17 February 1999

International Patent Classification (IPC) or both national classification and IPC

Int. Cl. 7 G11B 7/00, G03G 5/07, C08K 5/3417, 5/32, 5/23

Applicant

VICTORIA UNIVERSITY OF TECHNOLOGY et al

1. This written opinion is the **first** drawn by this International Preliminary Examining Authority.
2. This opinion contains indications relating to the following items:.

I	[X]	Basis of the opinion
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[X]	Lack of unity of invention
V	[X]	Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[X]	Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4*bis*.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: **17 June 2001**

Name and mailing address of the IPEA/AU	Authorized Officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	**J.W. THOMSON** Telephone No. (02) 6283 2214

WRITTEN OPINION | International application No. **PCT/AU00/00117**

Basis of the opinion

1. With regard to the **elements** of the international application:*

   [ ] the international application as originally filed.

   [X] the description, pages **1 - 12,** as originally filed,
   pages , filed with the demand,
   pages , received on with the letter of

   [X] the claims, pages , as originally filed,
   pages , as amended under Article 19,
   pages , filed with the demand,
   pages **13 - 20,** received on **23 June 2000**

   [X] the drawings, pages **1 - 6** as originally filed,
   pages , filed with the demand,
   pages , received on with the letter of

   [ ] the sequence listing part of the description:
   pages , as originally filed
   pages , filed with the demand
   pages , received on with the letter of

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
   These elements were available or furnished to this Authority in the following language which is:

   [ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

   [ ] the language of publication of the international application (under Rule 48.3(b)).

   [ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

   [ ] contained in the international application in printed form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readable form.

   [ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. [ ] The amendments have resulted in the cancellation of:

   [ ] the description, pages

   [ ] the claims, Nos.

   [ ] the drawings, sheets/fig.

5. [ ] This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*

WRITTEN OPINION

International application No.
PCT/AU00/00117

IV.	**Lack of unity of invention**

1. In response to the invitation (Form PCT/IPEA/405) to restrict or pay additional fees the applicant has:

   - [ ] restricted the claims.
   - [ ] paid additional fees.
   - [X] paid additional fees under protest.
   - [ ] neither restricted nor paid additional fees.

2. This Authority found that the requirement of unity of invention is not complied with for the following reasons and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees:

3. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

   - [X] all parts.
   - [ ] the parts relating to claims Nos.

WRITTEN OPINION

International application No.
PCT/AU00/00117

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	19, 21 - 25, 31, 33, 34, 45	YES
	Claims	1 - 18, 20, 26 - 30, 32, 35 - 44	NO
Inventive step (IS)	Claims	19, 21 - 25, 31, 33, 34, 45	YES
	Claims	1 - 18, 20, 26 - 30, 32, 35 - 44	NO
Industrial applicability (IA)	Claims	1 - 45	YES
	Claims		NO

2. Citations and explanations

US 5472759, US 5289407, US 5268862, and WO 9302454 each disclose the invention as defined in claims 1 - 18, 20, 26 - 30, 32

US 5744267 discloses photorefractive polymers having all of the features of claims 35 to 44.

US 5724460 discloses photorefractive polymers having all of the features of claims 35 to 38 and 40 and 41.

III. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 20 and 35 include within their scope the possibility of the photorefractive polymer being 100% polymer which applies no real limit on its composition.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 40351976 ROG JA	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. **PCT/AU00/00117**	International Filing Date *(day/month/year)* 16 February 2000	Priority Date *(day/month/year)* 17 February 1999

International Patent Classification (IPC) or national classification and IPC

Int. Cl. [7] G11B 7/00, G03G 5/07, C08K 5/3417, 5/32, 5/23

Applicant

VICTORIA UNIVERSITY OF TECHNOLOGY et al

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 9 sheet(s).

3. This report contains indications relating to the following items:

I	[X]	Basis of the report
II	[ ]	Priority
III	[ ]	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	[ ]	Lack of unity of invention
V	[X]	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	[ ]	Certain documents cited
VII	[ ]	Certain defects in the international application
VIII	[ ]	Certain observations on the international application

Date of submission of the demand 4 September 2000	Date of completion of the report 7 December 2000
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer **J.W. THOMSON** Telephone No. (02) 6283 2214

I. Basis of the report

1. With regard to the **elements** of the international application:*

   [ ] the international application as originally filed.

   [X] the description, pages **1 - 4, 6 - 12,** as originally filed,
   pages , filed with the demand,
   pages **5,** received on **24 November 2000** with the letter of **24 November 2000**

   [X] the claims, pages , as originally filed,
   pages , as amended (together with any statement) under Article 19,
   pages , filed with the demand,
   pages **13 - 15,** received on **23 June 2000**
   pages **16 - 20,** received on **24 November 2000** with the letter of **24 November 2000**

   [X] the drawings, pages **1 - 6,** as originally filed,
   pages , filed with the demand,
   pages , received on with the letter of

   [ ] the sequence listing part of the description:
   pages , as originally filed
   pages , filed with the demand

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
   These elements were available or furnished to this Authority in the following language which is:

   [ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

   [ ] the language of publication of the international application (under Rule 48.3(b)).

   [ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readable form.

   [ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. [ ] The amendments have resulted in the cancellation of:

   [ ] the description, pages

   [ ] the claims, Nos.

   [ ] the drawings, sheets/fig.

5. [ ] This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1 - 45	YES
	Claims	NO
Inventive step (IS)	Claims 1 - 45	YES
	Claims	NO
Industrial applicability (IA)	Claims 1 - 45	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

US 5472759
US 5289407
US 5268862
WO 9302454
US 5744267
US 5724460

These citations do not disclose the invention as defined in claims 1 to 45. In particular, they do not disclose a method of re-writable optical data storage using a photorefractive polymeric material to cause two-photon excitation.

25% - 99.5% of a polymer, such as PVK or PMMA;

0.5% - 60% of a chromophore, such as DMNPAA;

0.5%- 5% of a photosensitive material, such as TNF; and

0% - 40% of a plasticiser, such as ECZ.

Preferred embodiments of the present invention using cheap photorefractive polymers as recording materials for rewritable/erasable 3D bit optical data storage under two-photon excitation to produce a high-density 3D optical data storage system will now be described by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the absorption curve of a photorefractive polymeric material for use in the present invention;

Figure 2 is a schematic diagram of a two-photon excitation microscope used to record data bits in a photorefractive polymer;

Figure 3(a) is a 24 x 24 bit pattern of the letter "C" recorded by two-photon excitation in a photorefractive polymer PVK upon its first reading;

Figure 3(b) is the same region after reading 500 times;

Figure 3(c) is a 24 x 24 bit pattern of the letter "A";

Figure 3(d) is the same region as Figure 3(c) after being exposed to UV illumination showing complete erasure of the recorded information;

Figure 4 shows recorded 24 x 24 bit patterns at different depths in the photorefractive polymer PVK using two-photon excitation;

Figure 4(a) shows a first layer including letter "A";

Figure 4(b) shows a second layer including letter "B" and

Figure 4(c) shows a third layer including letter "C";

Figure 5 (a) is a bit pattern of the letter "E" recorded by two-photon excitation in another photorefractive polymer (PMMA).

Figure 5 (b) is the same region as Figure 5(a) after being exposed to UV illumination showing erasure of the recorded information;

Figure 5(c) is a bit pattern of the letter "F" written into the same area as Figures 1 and 2;

CLAIMS

1. A method of writing and erasing optical data comprising:

focussing light on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to record data; and

illuminating the material with radiation to erase the recorded data.

2. A method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing light on the photorefractive polymeric material to cause two-photon excitation of the material at the focal point thereby modulating the refractive index at the focal point to re-write data in the photorefractive polymeric material.

3. A method according to claim 1 or claim 2 wherein the modulation of the refractive index caused by the two-photon excitation is a refractive index inhomogeneity resulting from a non-uniform space-charge distribution within the region of excitation within the photorefractive polymeric material.

4. A method according to any one of claims 1 to 3 wherein the photorefractive material is illuminated with electro-magnetic radiation having a wavelength in the ultraviolet (UV) or visible spectrum to produce a redistribution of the spacial distribution of the electric charges forming bits of the data to erase the recorded data.

5. A method according to claim 4 wherein the photorefractive polymeric material is such that it absorbs radiation in only a narrow band in the UV to visible region of the electromagnetic spectrum.

6. A method according to claim 4 or claim 5 wherein the maximum of the absorption band of the photorefractive polymeric material falls substantially within the range from about 380nm to about 600 nm.

7. A method according to any one of claims 4 to 6 wherein the photorefractive polymeric material is such that is absorbs substantially no radiation above a wavelength of about 630 nm.

8. A method according to any one the preceding claims wherein the data recorded in the photorefractive polymeric material is read by illuminating the photorefractive polymeric material with coherent light of a wavelength falling substantially within the range from about 630 nm to about 1200 nm.

9. A method according to any one of the preceding claims wherein the light used to record data in the photorefractive material has a wavelength falling substantially within the range from about 750nm to about 1200 nm to cause two-photon excitation.

10. A method according to any one of the preceding claims wherein a pulsed laser beam is used to record data in the photorefractive polymeric material.

11. A method according to any one of claims 1 to 9 wherein a continuous wave laser beam is used to record data in the photorefractive polymeric material.

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12. A method according to any one of the preceding claims wherein polarised coherent light is used to record polarised bits of data in the photorefractive polymeric material.

13. A method according to claim 12 wherein different polarisation states of the recording beam are used to record multiple bits of data at the same position having different polarisation states in the photorefractive polymeric material.

14. A method according to claim 12 or claim 13 wherein bits of recorded data are read by using a reading beam having an appropriate polarisation state.

15. A method according to any one of claims 12 to 14 wherein individual bits of data are erasable by changing the polarisation state of the individual bits.

16. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

17. A method according to any one of the preceding claims, wherein the photorefractive polymeric material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

18. A method according to any one of the preceding claims wherein the photorefractive polymeric material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

19. A method according to any one of the preceding claims wherein the photorefractive polymeric material includs a plasticiser to reduce the glass transition temperature of the material.

20. A method according to any one of the preceding claims wherein the photorefractive material includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive material:

25% - 99.5% of a polymer ;
0.5%-60% of a chromophore;
0.5%-5% of a photosensitive material; and
0% - 40% of a plasticiser.

21. A method according to claim 16 or claim 20 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

22. A method according to claim 16 or claim 20 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

23. A method according to claim 17 or any one of claims 20 to 22 wherein the chromophore comprises 2, 5- dimethyl – 4 – (p-nitro-phenylazo) anisole (DMNPAA).

24. A method according to claim 18 or any one of claims 20 to 22 wherein the photosensitive material comprises 2, 4, 7-trinitro-9-fluorenone (TNF).

25. A method according to any one of claims 20 to 24 wherein the plasticizer comprises *N*-ethylcarbazole (ECZ).

26. A photorefractive polymeric optical data storage material for use in a method of erasable/rewritable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the photorefractive material is such as to enable the recording of bits of data by two photon

excitation, the reading of the bits of data by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band.

27. A photorefractive polymeric material according to claim 26 wherein the maximum of the absorption band of the photorefractive material falls substantially within the range from about 380 nm to about 600 nm.

28. A photorefractive polymeric material according to claim 26 or claim 27 wherein the upper end of the absorption band of the photorefractive polymeric material is about 630 nm.

29. A photorefractive polymeric material according to any one of claims 26 to 28 wherein the material includes at least about 25% of a polymer by percentage weight of the total weight of the photorefractive material.

30. A photorefractive polymeric material according to any one of claims 26 to 29 wherein the material includes a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum.

31. A photorefractive polymeric material according to claim 30 wherein the chromophore is present by an amount falling substantially within the range from about 0.5% to about 60% by percentage weight of the total weight of the material.

32. A photorefractive polymeric material according to any one of claims 26 to 31 wherein the material includes a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum.

33. A photorefractive polymeric material according to claim 32 wherein the photosensitive material is present by an amount falling substantially within the

range from about 0.5% to about 5% by percentage weight of the total weight of the photosensitive material.

34. A photorefractive polymeric material according to any one of claims 26 to 33 wherein the material includes a plasticiser to reduce the glass transition temperature of the material.

35. A photorefractive polymeric material according to claim 33 wherein the plasticizer is present by an amount falling substantially within the range from 0% to about 40% by percentage weight of the total weight of the photorefractive polymeric material.

36. A photorefractive optical data storage medium for use in a method of erasable/rewritable optical data storage in which light is focussed on the data storage medium to modulate the refractive index at the focal point by two-photon excitation, wherein the medium includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive data storage medium.

25% - 99.5% of a polymer;
0.5% - 60% of a chromophore;
0.5% - 5% of a photosensitive material; and
0% - 40% of a plasticiser.

37. A photorefractive optical data storage medium according to claim 29 or claim 36 wherein the polymer comprises poly (*N*-vinylcarbazole) (PVK).

38. A photorefractive optical data storage medium according to claim 29 or claim 36 wherein the polymer comprises poly (methyl methacrylate) (PMMA).

39. A photorefractive optical data storage medium according to any one of claims 30, 31 or 36 to 38 wherein the chromophore comprises 2,5-dimethyl-4-(p-nitro phenylazo) anisole (DMNPAA).

40. A photorefractive optical data storage medium according to any one of claims 32, 34 or 36 to 39 wherein the photosensitive material comprises 2, 4, 7-trinitro--9-fluorenone (TNF).

41. A photorefractive optical data storage medium according to any one of claims 34 to 40 wherein the plasticiser comprises *N*-ethylcarbazole (ECZ).

42. A photorefractive optical data storage medium adapted for use in a method of erasable/rewritable optical data storage in which light is focused on the data storage medium to modulate the refractive index at the focal point by two photon excitation, wherein the medium includes the following materials:

poly(*N*-vinylcarbazole) (PVK);
2,5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA)
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

43. A photorefractive optical data storage medium according to claim 42 wherein the PVK;DMNPAA;TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive material 33:50:1:16.

44. A photorefractive polymeric material for use in a method of optical data storage comprising the following materials:

poly (methyl methacrylate) (PMMA);
2, 5, dimethyl-4-(p-nitrophenylazo) anisole (DMNPAA);
2,4,7-trinitro-9-fluorenone (TNF); and
N-ethylcarbazole (ECZ).

45. A photorefractive polymeric material according to claim 44 wherein the PMMA: DMNPAA; TNF and ECZ are present in approximately the following concentrations by percentage weight of the total weight of the photorefractive polymeric material 73:10:1:16.